

Characterization of black crusts from the Monumental Cemetery (Milan) using a combined LIBS and Raman approach

A. Bergomi^a, V. Comite^a, C. Della Pina^a, P.M. Carmona-Quiroga^b, L. Maestro-Guijarro^b, M. Oujja^b, A. Crespo^c, C.A. Lombardi^a, M. Borelli^a, M. Castillejo^b and P. Fermo^a

^a Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133 Milano, Italy; ^b Instituto de Química Física Rocasolano, IQFR-CSIC, C/Serrano 119, 28006 Madrid, Spain; ^c Instituto de Estructura de la Materia, IEM-CSIC, C/Serrano 121, 28006 Madrid, Spain; andrea.bergomi@unimi.it

Black crusts represent one of the most dangerous degradation phenomena affecting stone materials of calcareous nature, which are very common substrates in architectural cultural heritage [1-2]. These layers of decay are generated from the interaction of the limestone substrate with atmospheric pollutants (SO₂ and particulate matter), which induces the chemical transformation of the substrate into gypsum in a process known as “sulphation”. The numerous studies conducted on the sulphation process in the last decades were able to unveil the chemical reactions responsible for the degradation, highlighting the catalytic role of carbonaceous particles incorporating several metal species commonly found in particulate matter (Fe, Mn, V, etc.). However, the mechanism of this process is not fully understood and the role of each metal in promoting the sulphation process is still unclear.

In the present study, black crust samples were taken from the Monumental Cemetery of Milan and characterized using Laser-Induced Breakdown Spectroscopy (LIBS) and Raman Spectroscopy [3]. The Monumental Cemetery of Milan is one of the largest and most renowned cemeteries in the city. It is known for its large number of tombs and monuments, which make it one of the symbols of the city and a popular tourist attraction. The site was officially opened in 1866 and therefore hosts hundred-year-old monuments which have been exposed through the years to a series of environmental pollutants that pose a threat to the conservation of cultural heritage. Indeed, Milan is one of the most polluted cities in Italy and the cemetery is in proximity to a very busy road, exposed to all the pollutants deriving from vehicular traffic.

Black crust formation was abundant in many of the sampled monuments and thanks to the use of the LIBS and Raman techniques it was possible to evaluate more than one-hundred years of pollutant accumulation. Specifically, the former technique was employed to evaluate the elemental superficial distribution and the in-depth metallic concentration profile from the outer part of the black crust to the substrate. Raman analyses were also carried out on different parts of the surface to highlight mineralogical transformations and the presence of organic substances. Moreover, thin sections of the black crusts were obtained and Raman mapping was performed to evaluate compositional differences between the different layers.

The results obtained from LIBS and Raman spectroscopies were compared to the ones from other analytical techniques (IC, SEM-EDX, TOT) and the combined data allowed for a complete characterization of the crusts' composition. This enabled to obtain a temporal registry of the crusts' formation that will be useful in the implementation of new protocols for the conservation of the architectural heritage of the Monumental Cemetery.

References:

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